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Electrodeposition of U and Pu on Thin C and Ti Substrates

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Abstract

Preparation of Pu and U targets on thin natural C (100 $\mu\text{g}/\text{cm}^2$) and Ti (2 & 3 μm) substrates is described. The actinide material of interest was first purified using ion exchange chromatography to remove any matrix contaminants or decay products present in the parent stock solution. The actinide solution was prepared in 0.05 M HNO_3 with a final aliquot volume not exceeding 100 μL for the deposition procedure. The electroplating cells were developed in-house and were primarily made of Teflon. The source material deposited ranged from 125 to 400 $\mu\text{g}/\text{cm}^2$. It was determined that multiple layers of U and Pu were required to produce thicker targets on Ti. Plating efficiency was greatly affected by the cell volume, solution aliquot size, pre-treatment of the foils, solution mixing during plating, and the fit of the electrode contact with the target substrate. The final procedure used for deposition is described in detail.

1. Introduction

Production of thin actinide targets is essential for determining various nuclear parameters associated with decay and fission events. The deposition layer of target material must be homogeneously distributed with a thickness relative to the type and efficiency of the reaction under observation and the beam (if applicable) characteristics. As an example, transactinide studies require thicker targets to produce sufficient product for study but still be able to withstand extended heavy ion beam bombardment over long time periods [1], while alpha spectrometry sources require a thin layer of material to minimize energy losses within the deposition [2]. Molecular deposition of actinides from organic media, such as isopropyl alcohol (IPA) is preferred for thin target production because of the relatively high plating efficiency and uniformity of deposition [3-5]. In this work, targets were prepared for neutron and light-ion bombardment experiments to examine capture cross-section measurements, surrogate cross-sections, and fission neutron spectra for various U and Pu isotopes. The target backing materials were thin C (60 to 100 $\mu\text{g}/\text{cm}^2$) or Ti (0.002 & 0.003 mm thickness, rolled) foils and the desired actinide deposition thickness was 125 and 400 $\mu\text{g}/\text{cm}^2$, respectively. The C foils presented a unique challenge due to the fragile nature of the foil. The Ti backed targets needed to be double-sided with uniform deposition over a large area (13 cm^2). The plating cells designed in-house to produce these targets are described.

Actinide target fabrication for cross-section measurements requires the use of high purity actinide salts. In this work, the parent actinide solutions are purified by ion exchange chromatography to remove decay products and other potential matrix contaminants. The parent solutions were in HCl or HNO_3 prior to purification and the primary contaminants of concern were Th and U. A detailed description of the purification chemistry is provided.

2. Experimental

2.1 Chemical Purification of U and Pu Salts

Ion exchange chromatography was used to purify both U and Pu salts prior to electrodeposition. The U material was dissolved in 8 M HNO_3 , and was loaded onto a pre-conditioned anion exchange resin (Bio-Rad AG-1-X8, 100-140 mesh) column. Under these conditions, U passes through the column while Th and some other daughter products were retained. The column was rinsed with several column volumes of 8M HNO_3 and the eluate collected in a glass centrifuge tube. The solution was evaporated to dryness in a water bath, and converted to a chloride salt using HCl. The salt was reconstituted in 9M HCl, which was loaded onto a separate anion exchange resin (AG-1-X8, 100-140 mesh) column. The column was rinsed with several column volumes of 9 M HCl to remove residual Th, then the U eluted with 0.1 M HCl. A few drops of concentrated HNO_3 were added to the purified U solution during evaporation to convert to the nitrated salt form. The salt was re-dissolved in 100 to 500 μL of 0.05 M HNO_3 and the solution assayed using alpha spectrometry to determine the final volume required for target production.

The Pu salt was dissolved in a concentrated HCl/HI mixture and evaporated to dryness. The residue was reconstituted in concentrated HCl with a few drops of concentrated HNO_3 , then evaporated to dryness again. These steps were repeated twice, and Pu was precipitated from HCl using NaOH. The precipitate was redissolved with a minimum volume of 9 M HCl and a few drops of concentrated HNO_3 . The solution was loaded onto a pre-conditioned anion exchange resin (AG-1-X8, 100-140 mesh) column and rinsed with 9 M HCl. Plutonium was retained under these loading conditions, while the daughter products and other contaminants were eluted from the column. A concentrated HI/ 10 M HCl (1:12 ratio by volume) eluent was used to remove Pu from the column. The solution was collected in a glass centrifuge tube and evaporated to dryness in a water bath. The salt was reconstituted in a minimum volume of 8 M HNO_3 and a drop of saturated NH_4NO_2 was added to adjust to the Pu^{4+} oxidation state. The solution was loaded onto a separate pre-conditioned anion exchange resin (AG-1-X8, 100-140 mesh) column and additional 8 M HNO_3 used to rinse the column. The resin column was converted to the Cl^- form using 9M HCl, then Pu eluted with concentrated HI / 10M HCl

(1:12 ratio by volume). The Pu was taken to dryness with the addition of a few drops of concentrated HNO_3 to convert to the nitrate salt form, dissolved in a minimum amount of 0.05 M HNO_3 and then assayed using alpha spectrometry to determine the aliquot size needed for the desired target thickness. For ^{239}Pu the source material was 99.957% ^{239}Pu . The pre- and post-separation alpha spectra area shown in Figure 1 and Figure 2, respectively. While these are not highly informative in themselves, it is noted that the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio improved from its initial value of 0.0103 ± 0.0006 (2σ) to 0.0025 ± 0.0009 most likely due to the removal of any residual ^{241}Am .

2.2 Target Production

2.2.1 Electrodeposition on Thin C Foils

An electroplating assembly was designed to accommodate a 60 to 100 $\mu\text{g}/\text{cm}^2$ C foil, 1.27 cm diameter plating area, mounted on an Al support frame (Figure 3). The base (1) and clamp plates (6) are Al and the chimney (5) and support plate (2) are Teflon. The plating cell volume is defined by the chimney dimensions, which are 1.27 cm bore x 5 cm height, giving a total volume of 6.3 ml. A Viton o-ring (4) was used to maintain the seal between the chimney and pre-mounted target support frame (3). Two alignment rods in the base plate positioned the chimney onto the target frame so that the amount of the frame exposed during plating was minimized. A milled depression in the Teflon support plate, not shown in Figure 3 accommodated the Al target frame, providing perfect alignment between the chimney and the target substrate. The assembly was gently compressed using four pan head machine screws, which were initially pre-tensioned across the diagonal and then rotated half turns sequentially until the assembly was locked in place. The plating power supply (GW Instek model GPR-30H10D, 300W, capable of delivering maximum values of 300V at 1A) operated in a constant current mode (4 mA, corresponding to a current density of 3.2 mA/cm^2 for a 1.27 cm diameter target) and the leads were attached to the Pt wire anode and the Al target frame. The Pt wire had a small coil at the end and was suspended just above the substrate to promote even deposition of the actinide.

The carbon foil was floated off the glass slide onto an Al target frame using distilled water, and then allowed to dry at room temperature overnight. A second target frame of the exact same dimensions was coated with a fine spray of organic adhesive (3M 77-Multipurpose Adhesive) and the two target holders were pressed together. The C foil became affixed to the new target frame. This method was developed as an alternative to direct pickup from the carbon slides. When trying to lift the carbon foils directly from the glass slides they would shatter or tear with almost 100% failure. The 60 $\mu\text{g}/\text{cm}^2$ C targets were very fragile and ruptured easily both before and during plating using this mounting technique; therefore, only the 100 $\mu\text{g}/\text{cm}^2$ C foils were prepared for cross section studies. The loaded target support frame was slid into the milled section of the Teflon plate. This motion evenly distributes the lateral force while minimizing the perpendicular force on the foil to help prevent rupture. Once assembled, the deposition cell was pre-treated with IPA (approximately half the chimney volume, about 3 ml) to check for leaks. An aliquot of the purified actinide solution was added to the assembled cell and the solution was mixed with a transfer pipette prior to deposition. Electroplating was carried out at ambient conditions. There was not any attempt to control the temperature of the plating cell, substrate, or solution. A deposition time of 1 hour was used for both U and Pu target fabrication. No systematic study has been performed to determine the optimal electroplating conditions using this apparatus. Plots of the current and voltage values observed during a typical plating process on a 100- $\mu\text{g}/\text{cm}^2$ 1.27 cm C substrate are shown in Figure 4 for Pu and Figure 5 for U. In these cases the current remained constant and the voltage varied during the electroplating process. At the end of the plating process, the remaining IPA solution was removed from the cell with a transfer pipette and the cell was disassembled. The Al target frame was pushed horizontally across the Teflon support plate until the C foil was completely exposed on both sides, then the Al frame was placed on edge into a plastic 50 mL centrifuge tube to dry. The Al frame fit securely into the tube and prevented surface contact with the C foil. No heat was applied to the foil post deposition due to the fragile nature of the backing material.

2.2.2 Double-Sided Electrodeposition on Thin Foils

An example of the plating cell used for deposition of actinides on both sides of a metal substrate is provided (Figure 6). The blocks were milled from Teflon and the electrodes were Pt (25.4 x 25.4 x 0.051 mm). Two forms of the cell were utilized, one for 4-cm diameter depositions and the other for 7-mm diameter depositions. For the 4-cm diameter depositions each cell half has a total volume near 48-ml, which was not completely filled, nominally about 40-ml of solution were used on each side. For the final design of the 7-mm cell, each cell half contained about 9-ml of solution, which again was not completely filled, so about 15-ml of total solution was used in the entire cell. The Ti target foil was positioned using the grooves milled into the two inner Teflon blocks and held in place by o-rings. The grooves allow for position reproducibility should multiple layers be required to achieve the desired target thickness. The outer and inner Teflon blocks were pre-assembled with the Pt anodes prior to loading the target foil. Once the foil was positioned on one half of the cell, a Pt cathode was placed so that electrical contact was maintained between the power supply and the foil. The second half of the cell was positioned and fixed in place with cap screws. The power supply was set at a constant current (3 mA/cm² target) and the two anodes were connected by a jumper cable. Solution mixing was kept constant using a peristaltic pump (ISMATEC Reglo-Digital, 100 rpm) throughout the deposition procedure. The pump tubes are Tygon, fitted with short PEEK or FEP Teflon stubs used to pump the IPA solution to and from the cell. The IPA solution was pumped from the bottom of the cell and returned to the top. The solutions in each cell remained independent of one another. Despite the relatively inert surface of the Teflon material, following an electroplating run using Pu, some material was found to have deposited onto the surface, whether by precipitation or adsorption. Some material was also deposited inside the peristaltic pump tubes during the electroplating process. No quantitative measure of the lost material was taken.

Once the cell was assembled, IPA and a 100 μ L aliquot of 0.05 M HNO₃ were added to the solution wells and mixed for 30 minutes. This process cleaned the substrate prior to plating. The cleaning solution was removed from each cell and the IPA and actinide solution aliquot were added. The solutions were equilibrated for 30 minutes, followed by a 1 hour deposition. As noted above, no systematic study into the optimum plating

conditions has been performed using this apparatus. The pump was used to remove the remaining plating solution and the cell was disassembled. The target foil was placed in a glass evaporation dish for secondary containment and was heated on a hot plate for at least 1 hour. The deposition thickness was determined by gamma spectrometry, assuming equivalent plating efficiency.

3. Results and Discussion

3.1 Thin C Targets

The thin natural C targets presented a unique production challenge. The material was very fragile, with a 40% rupture rate during plating. Most tears occurred at the interface between the target support and the C foil. The foils were mounted to the target frames using a floating technique, which created a rippled surface (Figure 9) and may have contributed to the failure of the films. The plated U targets were bright yellow, with the material concentrated along the ridges in the foil (Figure 10, top). Plutonium deposition was more homogeneously distributed across the surface of the foil (Figure 10, bottom) and was black in appearance. The targets were not quantified by alpha spectrometry; however, the remaining IPA/HNO₃ solution was evaporated to near dryness and then assayed to determine the amount of actinide remaining in solution. Due to concerns about the strength of the C foils involved, these targets were not directly assayed prior to use in the experiment that they were created for. The customers were using these targets for relative reaction rate studies, where the exact amount of material on the target was relatively unimportant, however it is estimated that a near quantitative transfer of 125 µg/cm² of either U or Pu on target was achieved in a single plating using this process.

3.2 Double Sided Targets

Ti foils were used for double-sided target production. These foils did not rupture during plating, and a thickness of 400 µg/cm² (per side) was produced with two successive depositions. For U targets with a 4 cm diameter plated area, the first deposition resulted in a nominal thickness of 300 µg/cm². The foil was baked on a hot plate at moderate heat, to eliminate any concern for burning of the Ti foil, for several hours, then assayed

by gamma spectrometry. The foil was reloaded in the Teflon cell, using the alignment grooves to aid positioning of the foil, and the procedure was repeated with the final 100 $\mu\text{g}/\text{cm}^2$ of U dissolved in a minimum volume of 0.05 M HNO_3 ($< 100 \mu\text{L}$). The surface of the target appeared to be smooth with an iridescent sheen where the U was deposited (Figure 11). A total of eleven foils have been produced by this method with similar results.

A 2- μm Ti foil containing 500 $\mu\text{g}/\text{cm}^2$ (per side) of Pu in a 7-mm diameter deposition area was produced in four successive depositions. The first three layer was to be 100 $\mu\text{g}/\text{cm}^2$, but only 70% of the material deposited. The second layer was to add 200 $\mu\text{g}/\text{cm}^2$, but only 17% on the material deposited. Additional fresh material had not been prepared, so the 'spent' IPA solution was put back into the cell and electroplating proceeded for a period of three hours. A total of 30% of the second aliquot was deposited, resulting in total layer thickness of 130 $\mu\text{g}/\text{cm}^2$. After each deposition, the foil was gently baked for several hours, placed in secondary containment and assayed by gamma spectrometry. After each assay, the secondary container was checked for activity. The amount of activity present in the container was significant compared to that observed for the U targets, suggesting decreased mechanical stability of the plated material. The cause of the poor plating efficiency was traced to the initial design of this cell, which was a simple modification of the U target plating cell with the diameter of the plating area reduced from 4 cm to 7 mm. Due to the flexibility of the Teflon material and the distance to the clamping screws, the Pt cathode disk used to make electrical contact with the Ti target foil fit very loosely in the apparatus. The inner section of the cell were re-fabricated, relocating the plating area to within 1.2 cm of the top of the cell and reducing the total fluid volume from about 96 ml to 18 ml. The electrodes were re-fitted into the modified cell. The target was reloaded into the cell and an aliquot volume equivalent to 300 $\mu\text{g}/\text{cm}^2$ and IPA were added to each solution well. After the final deposition, gamma assay estimated a 500 $\mu\text{g}/\text{cm}^2$ thickness on each side of the target. The extra deposited material was assumed to be from the contaminated Pt anodes that were used in the previous design and were not cleaned prior to the final deposition, although the exact source is not known. The final target was black in appearance and produced far less contamination in the secondary container, indicating better adhesion

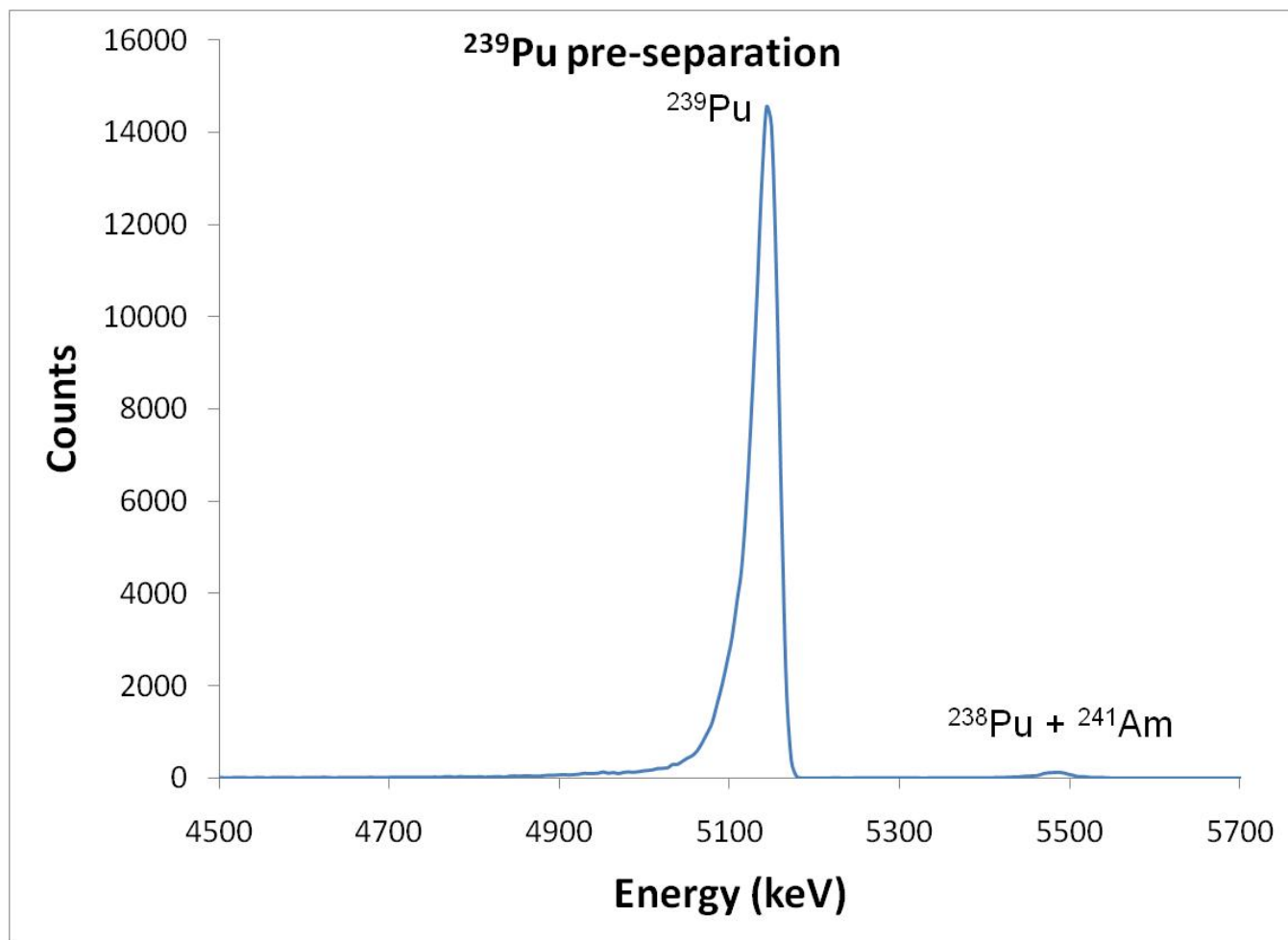
to the Ti substrate. More Pu targets will be produced in the future, but due to the activity of the desired deposit, the work will have to be performed in a glovebox. This has necessitated a new design for the center clamping mechanism, as there is not sufficient dexterity to handle the cap screw, washers, and nuts with the current design.

4. Summary

The chemistry and electrodeposition cells described in this work are suitable for producing high purity actinide targets on thin C and Ti foils. The double-sided cell design is currently being modified for a glovebox environment so that other actinides of interest can be electrodeposited on these films. The electrodeposition cell for the thin C foils produced a fairly homogenous distribution of both Pu and U; however, the process needs to be optimized to reduce the failure rate (i.e. target tearing). A separate technique is being developed for mounting the C foils on the Al frames. These foils will be tested in the electrodeposition cell prior to any structural modification.

5. Acknowledgements

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255 Figure 1. Alpha spectrum of the Pu source solution prior to chemical separation to
256 remove radiogenic daughter nuclides

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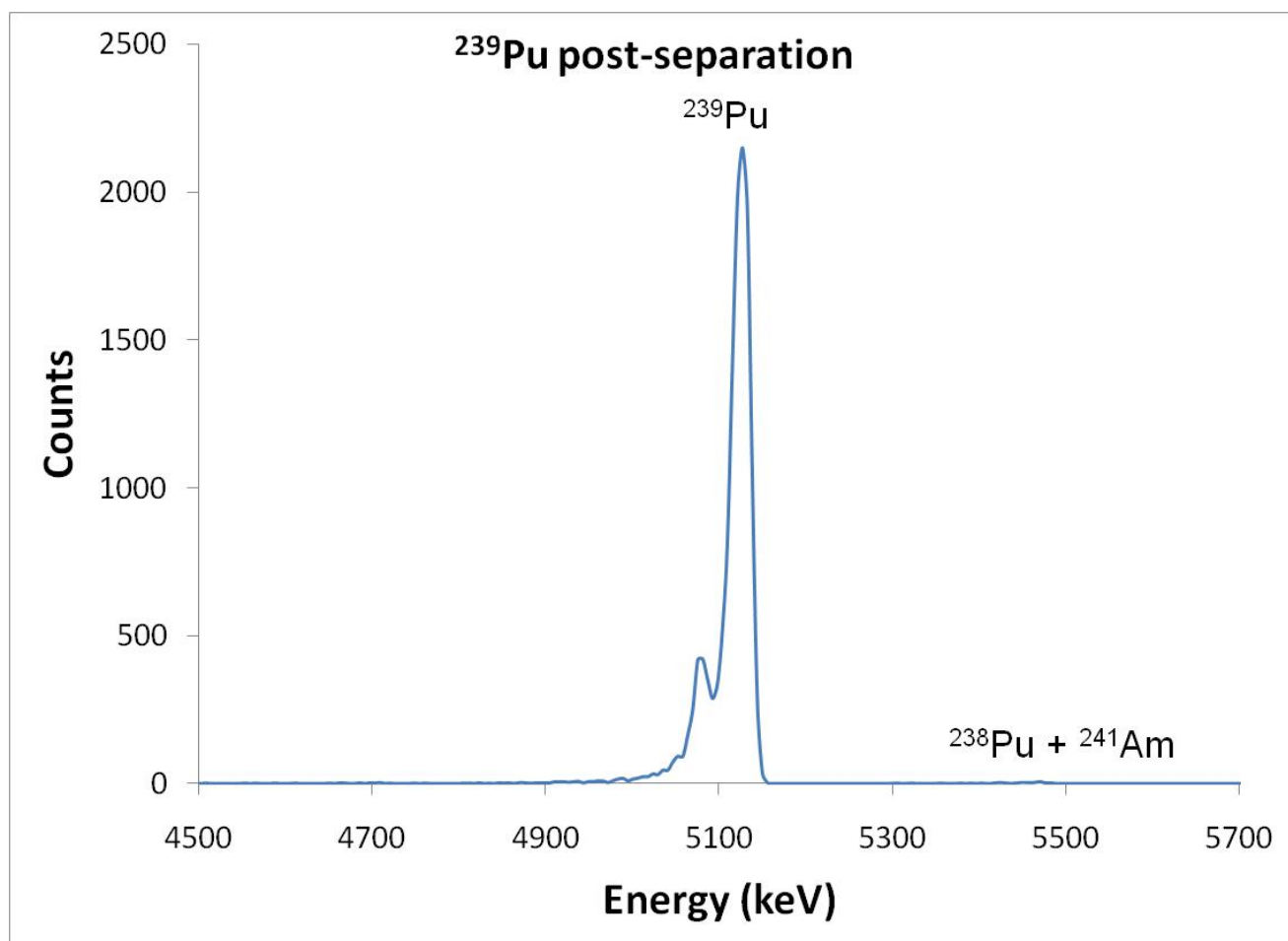


Figure 2. Alpha spectrum of the Pu solution after chemical separation

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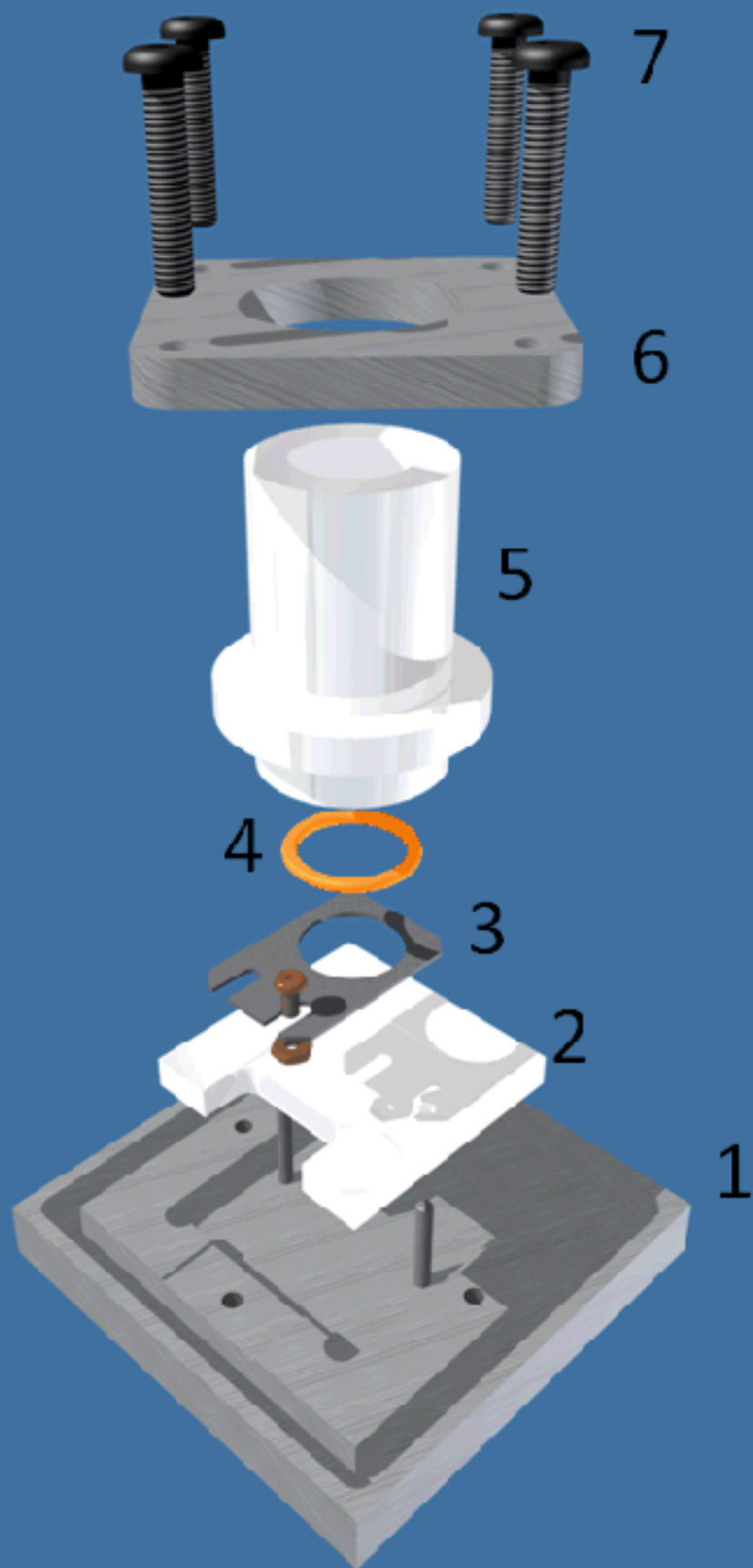


Figure 3 Electrodeposition cell for actinides

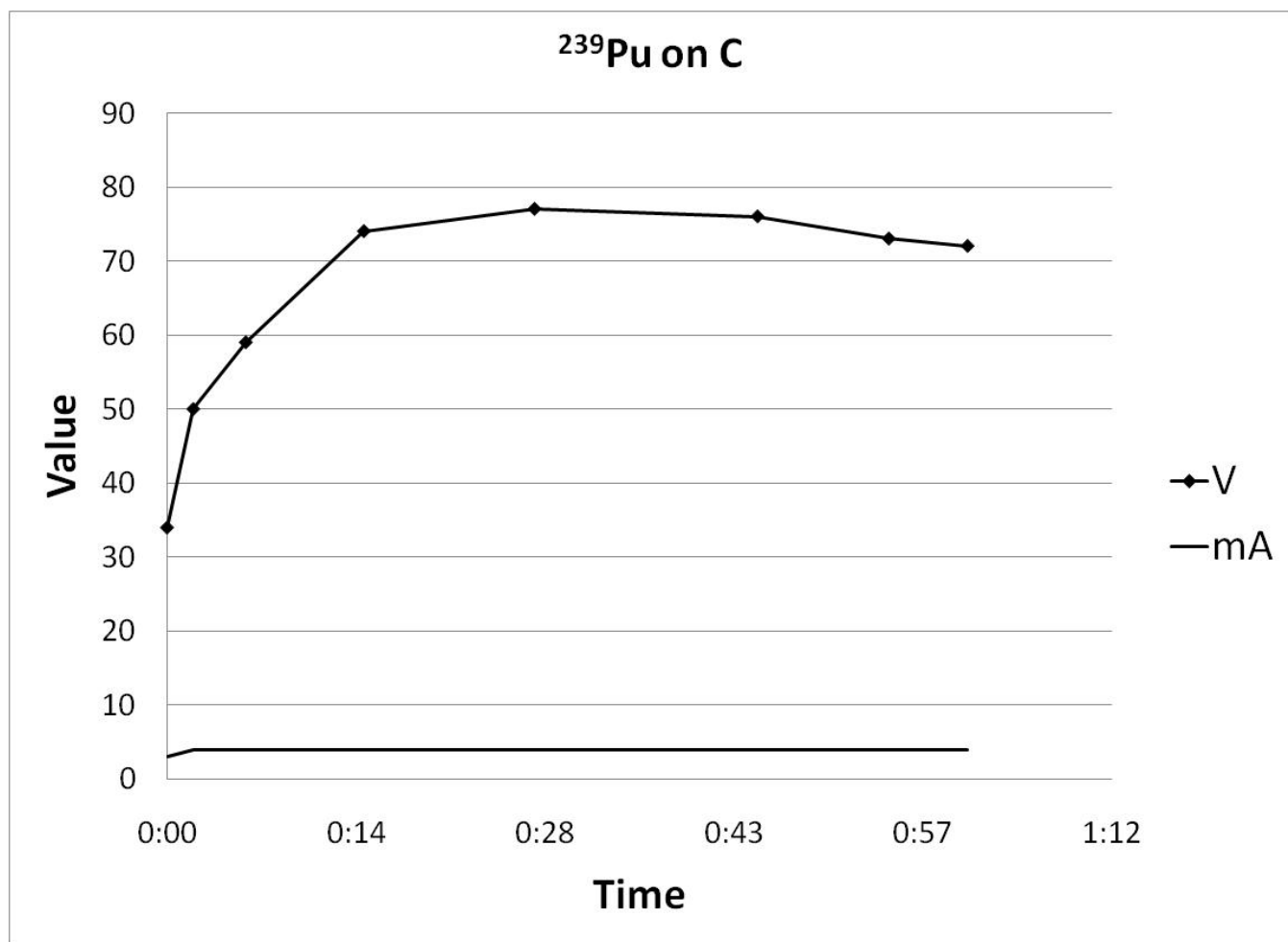


Figure 4. Plot of typical voltage (V) and current (mA) values during plating of Pu on a 1.27 cm $100\text{ }\mu\text{g}/\text{cm}^2$ C substrate from about 3 ml of isopropanol solution containing less than $100\text{ }\mu\text{l}$ of aqueous Pu-nitrate solution (in 0.05M HNO_3).

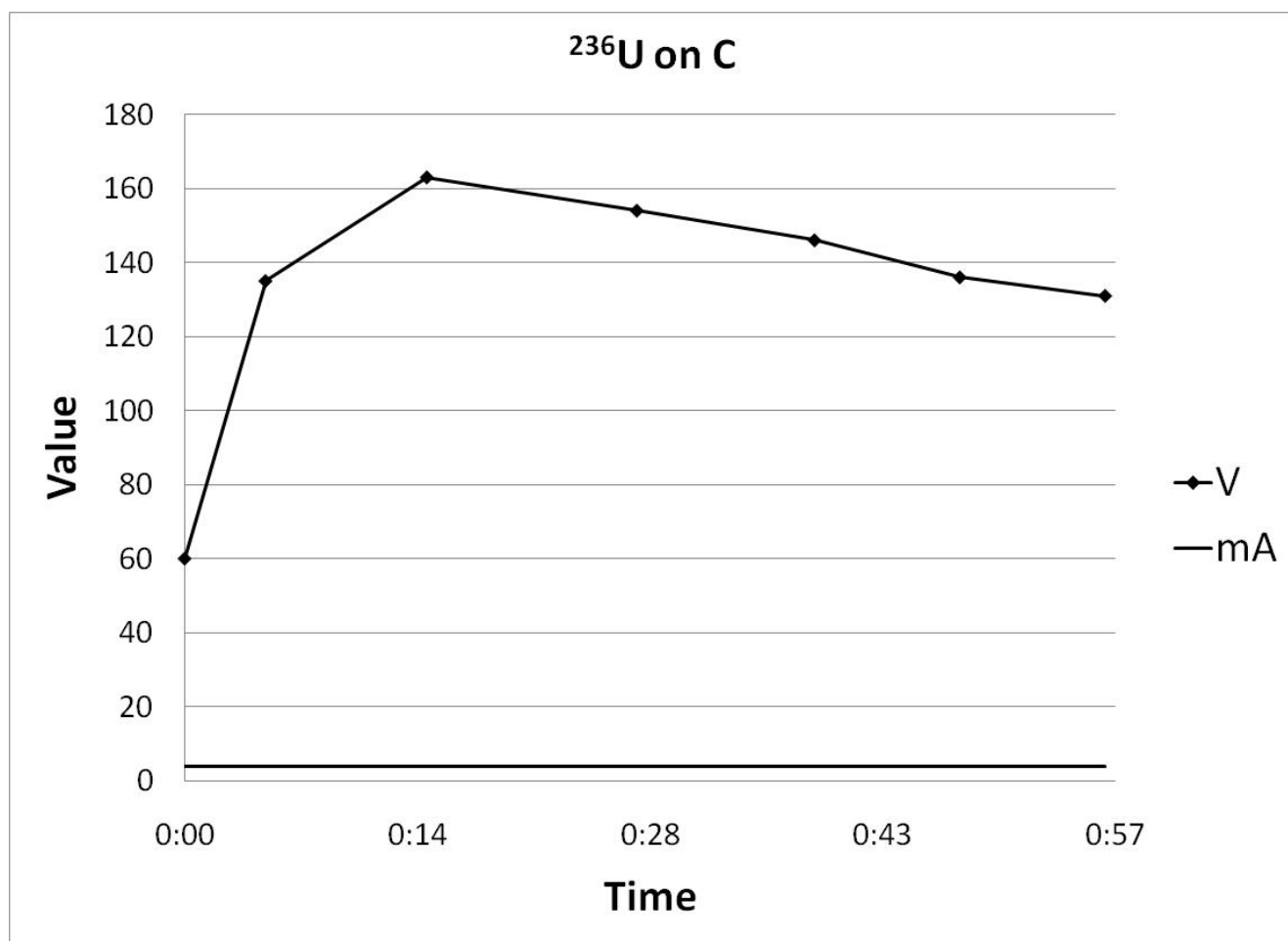


Figure 5. Plot of typical voltage (V) and current (mA) values during plating of U in a 1.27 cm diameter deposit on $100\text{ }\mu\text{g}/\text{cm}^2$ C substrates from about 3ml of isopropanol containing less than $100\text{ }\mu\text{l}$ of aqueous Uranyl-nitrate solution (in 0.05M HNO_3).

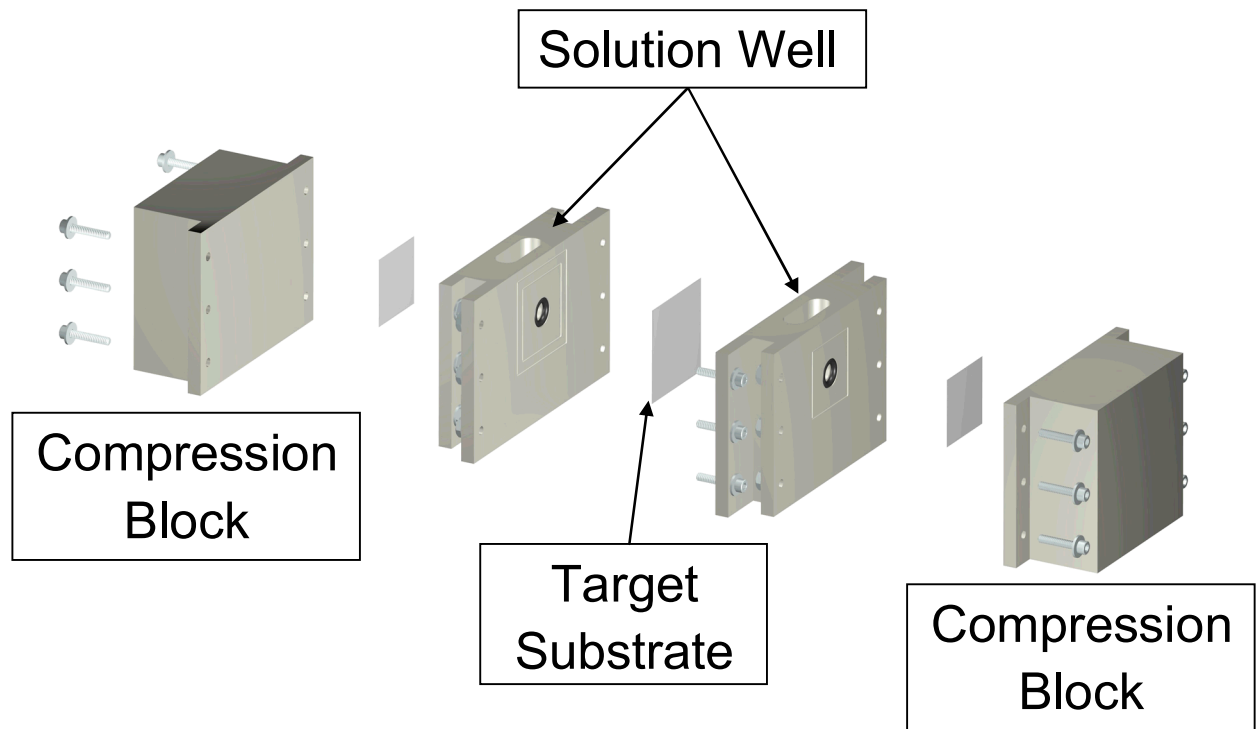


Figure 6. Schematic of the double sided electrolytic cell.

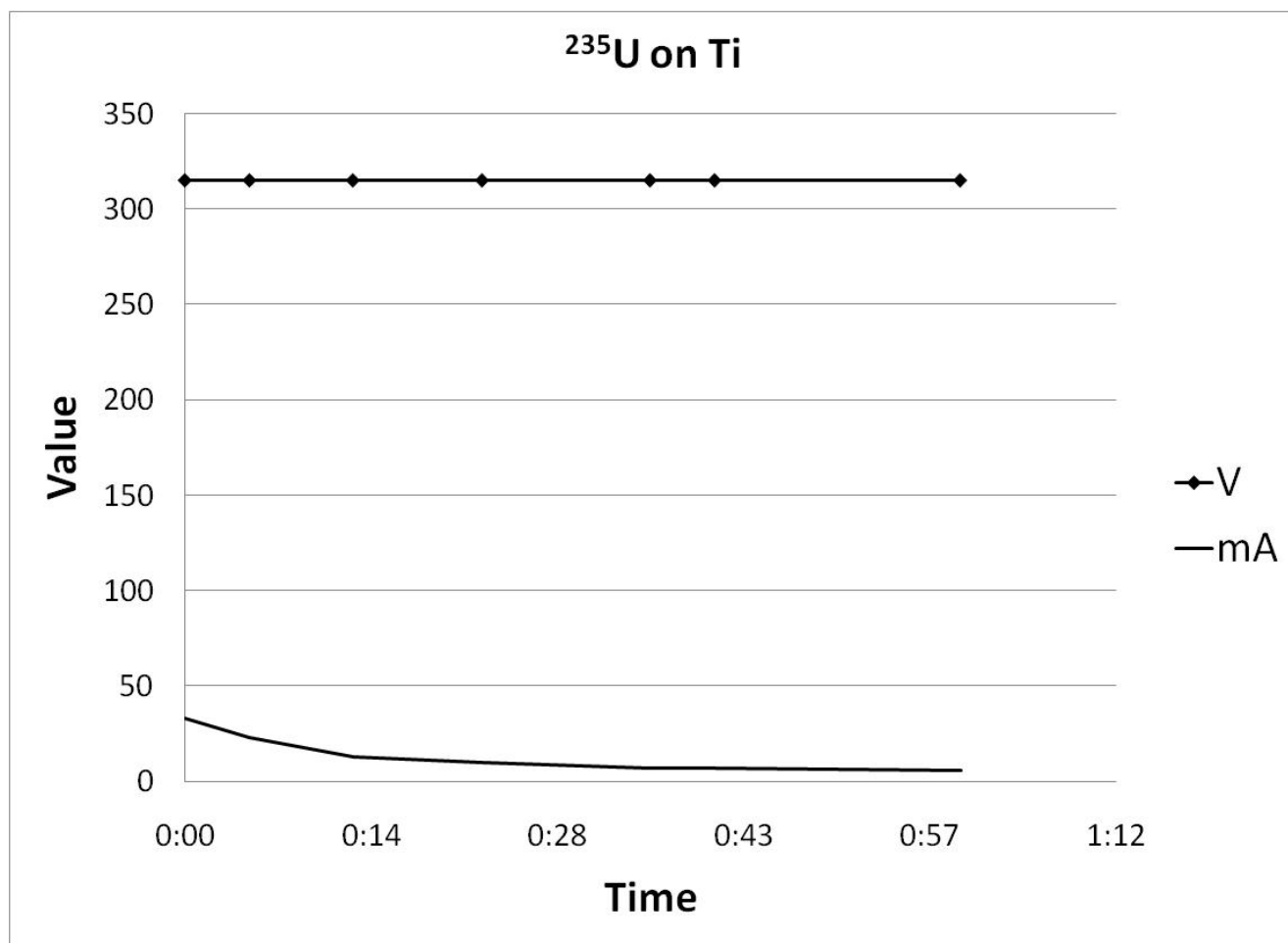


Figure 7. Plot of voltage (V) and current (mA) values observed during the plating of U on both sides of a 3 μm Ti substrate. The deposit is 4 cm in diameter. The cell volume is about 35 ml on each side, and U is introduced into the IPA solution using a volume less than 100 μl in 0.05M HNO_3 .

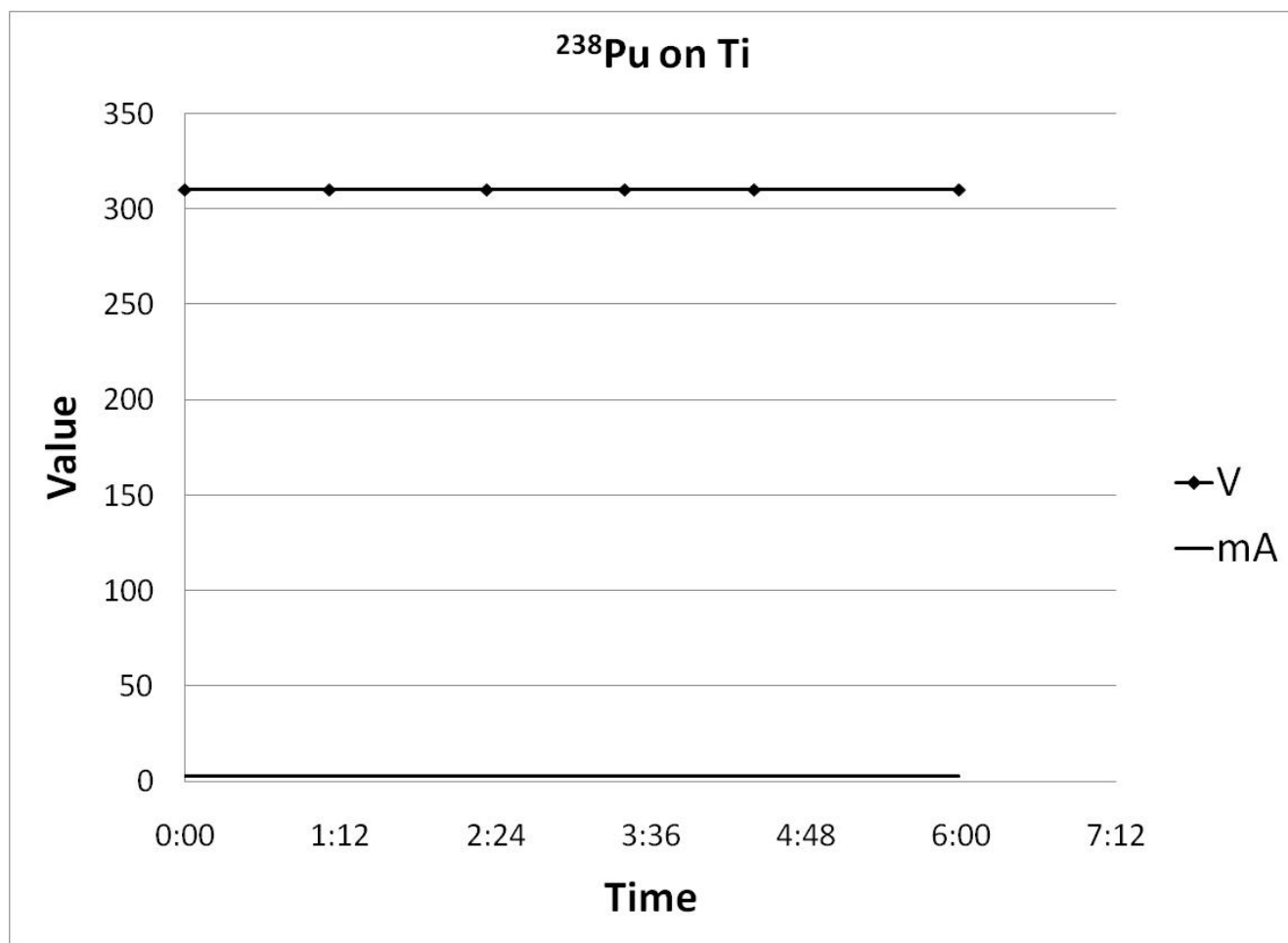
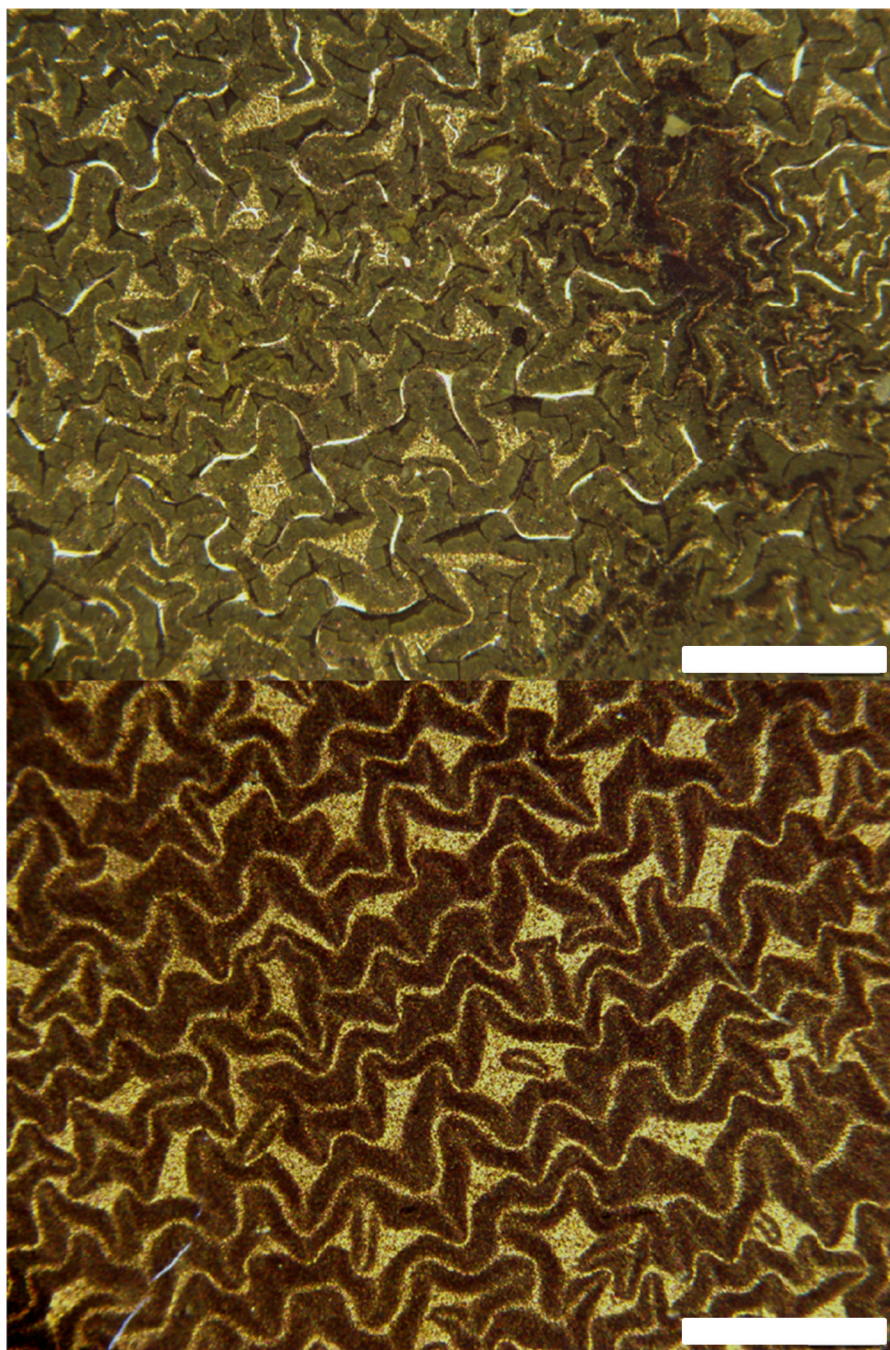


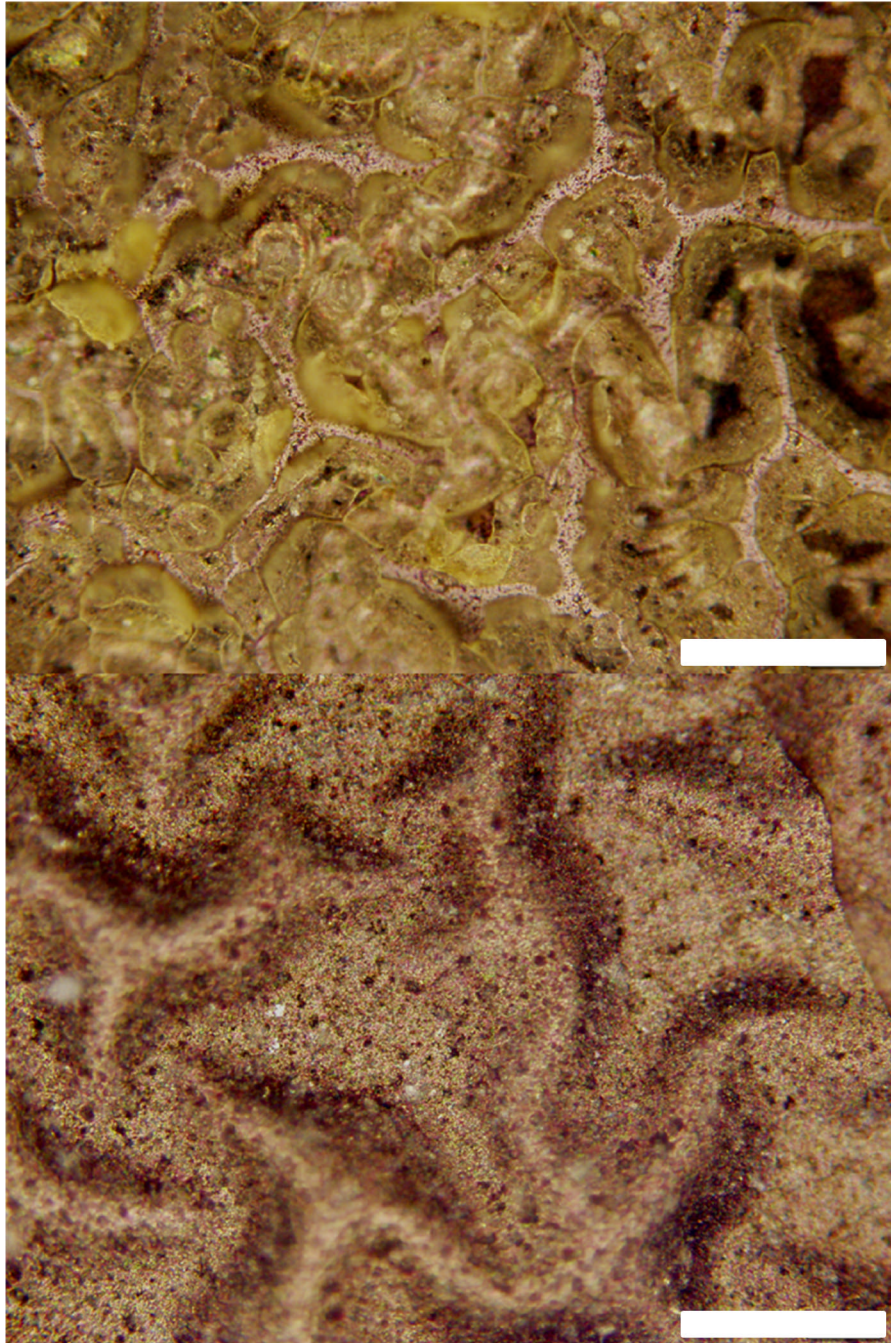
Figure 8. Plot of voltage (V) and current (mA) values for plating of Pu on both sides of a 3 mm Ti substrate. The deposition diameter is 7 mm. Each side of the electroplating apparatus has a volume of about 15 ml. The Pu to be electroplated is introduced in less than 100 μ l of 0.05M HNO₃.



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311 Figure 9. Surface of thin C foils after plating U (top) and Pu (bottom). Images were
312 obtained with a petrographic microscope. Scale bar is 500 μm.

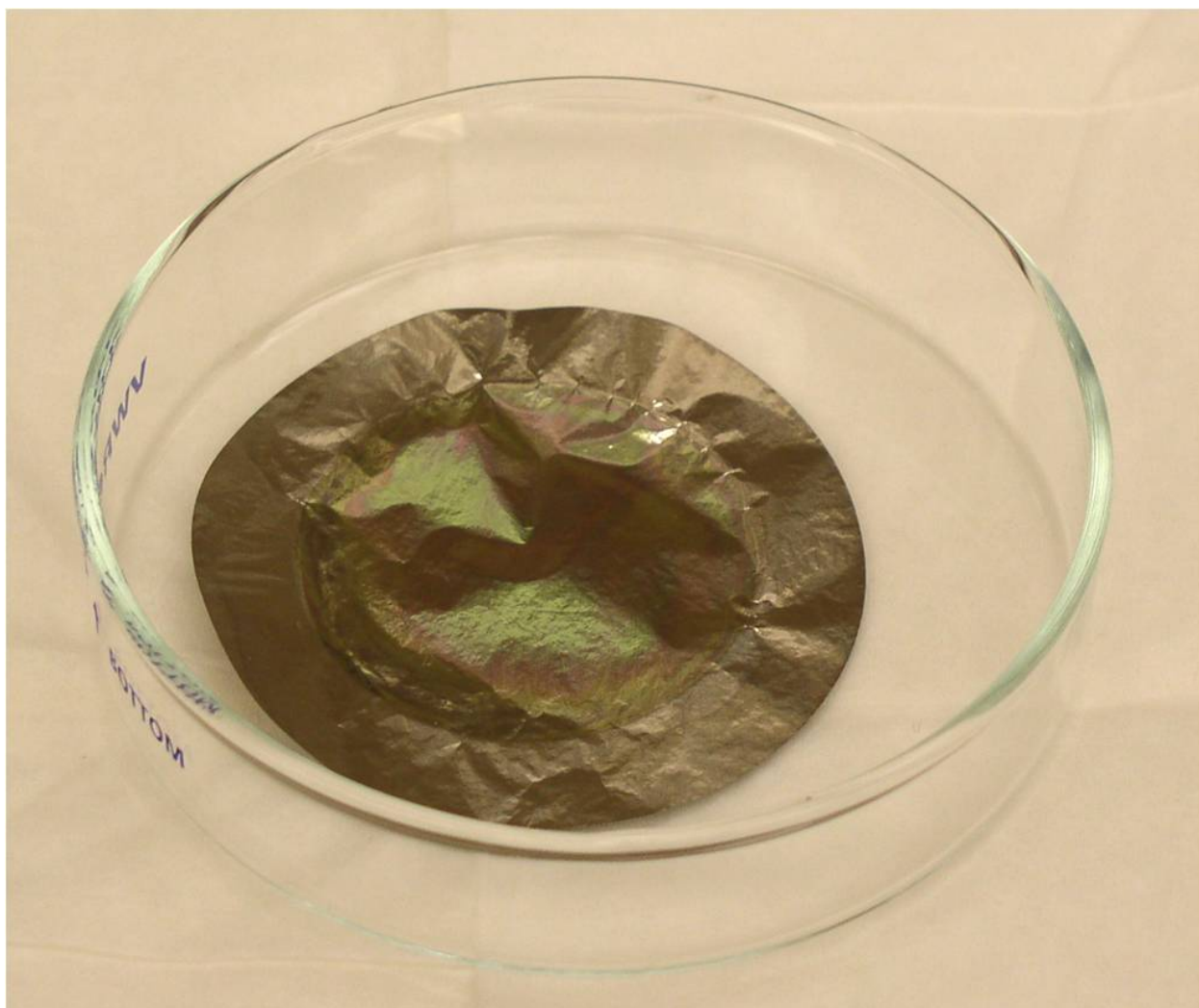
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315 Figure 10. Uranium (top) and Pu (bottom) deposition on thin C-foils. Images were
316 obtained with a petrographic microscope. Scale bar is 125 μm .

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319 Figure 11. Thin Ti foil with $400 \mu\text{g}/\text{cm}^2$ of U deposited on the surface.

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